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PREPARATION OF SEVERAL NEW TRANSITION METAL HYDRIDO COMPLEXES OF A TYPE MH(Y)L_n (M = Ni, Pd, Pt; Y = IMIDO, ALKENYL CARBOXYLATO) AND ELIMINATION OF HY FROM THE COMPLEXES ON INTERACTION WITH π -ACIDS

Takakazu YAMAMOTO,* Kenji SANO, and Akio YAMAMOTO Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

MH(succinimido) $(PCy_3)_2$ (M = Ni, Pd) and <u>trans</u>-PtH(OCOR) $(PCy_3)_2$ (R = -C(CH₃)=CH₂, -CH₂CH=CH₂) have been prepared by oxidative addition of succinimide or the corresponding acid to the zerovalent transition metal complexes. Treatment of the hydrido complexes with π -acids such as CO and maleic anhydride causes elimination of succinimide or RCOOH.

Transition metal hydrides are regarded as key intermediates in various transition metal catalyzed reactions. From this view point, a number of transition metal hydrides as the model compounds for the active intermediates have been prepared by various methods, and reactivities of the transition metal hydrides have been extensively studied.¹⁾ We now report preparation of several new transition metal hydrides of a type $MH(Y)L_n$ (M = Ni, Pd, Pt; Y = succinimido, OCOR) by oxidative addition of HY to M(0)-complexes (Eq. 1) and elimination of HY induced by π -acids such as CO and maleic anhydride (Eq. 2),

 $ML_{m} + HY \longrightarrow MH(Y)L_{n} \qquad (1)$ $MH(Y)L_{n} + \pi - acid \longrightarrow M(\pi - acid)L_{n} + HY \qquad (2)$ $\pi - acid = CO, maleic anhydride, etc.$

In spite of numerous reports on the reactivities of transition metal hydrides, only a few reports²⁾ have been published on the elimination of HY. Preparation of New Transition Metal Hydrides.

When a THF solution containing 510 mg (1.85 mmol) of Ni(cod)₂ (cod = 1,5cyclooctadiene), 1.04 g (2 mol/Ni) of tricyclohexylphosphine (PCy₃), and 183 mg (1 mol/Ni) of succinimide was stirred for 1 day at room temperature, a yellow precipitate was formed. The yellow solid was washed with diethyl ether and recrystallized from CH_2Cl_2 to yield 1.1 g (74%) of <u>trans</u>-NiH(succinimido) (PCy₃)₂, 1. A similar reaction of Pd(PCy₃)₂ with succinimide affords PdH(succinimido) (PCy₃)₂, 2. Roundhill³ reported that reactions of Pd(PPh₃)₄ with imides did not afford the PdH(imido) type complexes but the reactions gave Pd(imido)₂ type complexes. Isolation of 2 is the first example of isolation of an oxidative addition product formed by the reaction of an N-H compound with a Pd complex. Reactions of Pt(cod)₂ with unsaturated acids in the presence of PCy₃ also afford the oxidative addition products, trans-PtH(OCOC(CH₃)=CH₂)(PCy₃)₂, 3, and trans-PtH(OCOCH₂CH=CH₂)(PCy₃)₂, 4. Formation of a Pt-containing cyclic ester type complex in the reaction was not observed in contrast to the previously reported formation of metallacyclic esters in reactions of the unsaturated carboxylic acids with analogous zero-valent Ni^{4,5)} and Pd^{5} complexes. Although preparation of PtH(OCOR)L type complexes by oxidative addition of saturated carboxylic acids has been reported, 1,6) preparation of a similar complex having an unsaturated carboxylato ligand has no precedent.

Complex ^{a)}	Yield %	Color	mp °C	C A	nalysis H	b) N	$\frac{\mathrm{IR}^{\mathrm{C}}}{\mathrm{cm}^{-1}}$
trans- H-NiL ₂ -N L C-CH ₂ C-CH ₂ C-CH ₂	74	yellow	165- 170 (dec)	66.8 (66.9)	10.6 (9.9)	1.9 (2.0)	1990* 1620**
H-PdL ₂ -N C-CH ₂ 2 C-CH ₂	15	white	212- 214 (dec)	62.6 (62.7)	10.1 (9.3)	1.8 (1.8)	2040* 1630*
$\frac{\text{trans}}{\text{H-PtL}_2-\text{OC-C=CH}_2}$	34	white	245- 247	57.0 (57.0)	9.1 (8.7)		2240* 2200* 1590**
$\overset{\text{trans-}}{\underset{4}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{CH=CH}}{\overset{\text{O}}{\overset{\text{CH=CH}}{\overset{\text{O}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{O}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{O}}{\overset{\text{CH}}{\overset{\text{O}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}{\overset{\text{CH}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	36	white	154- 155	56.8 (57.0)	9.0 (8.6)		2240* 2220* 1620**

Table 1. Analytical and IR Data of Complexes 1-4.

a)	$L = PCy_3$.	b)	Calculated	value	in	parentheses.	c)	*	ν (M- H).	**	ν (C=O)).
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Table 2. NMR Data of Complexes 1-4.^{a)}

Complex	¹ H-NMR (δ, ppm) ^b)	$ \begin{array}{c} 13 \\ C \left\{ {}^{1} \\ H \right\} - NMR \\ (ppm from TMS) \end{array} $	$\frac{31}{P}\left\{ {}^{1}H\right\} - NMR$ (ppm from external PPh ₃)
1~	-23.2(lH,t,8Hz,Ni-H) 2.36(4H,s,CH ₂)	32.32(CH ₂)	
2~	-13.6(lH,s,Pd-H) 2.80(4H,s,CH ₂)		47.1
3	-22.7(lH,t,l4Hz,Pt-H)* 1.7(3H,m,CH ₃) 5.09(lH,=CH ₂) 5.71(lH,=CH ₂)	20.53(CH ₃) 118.53(=CH ₂) 144.27(OCO <u>C</u> =) 171.71(O <u>C</u> O)	46.7 (J(¹⁹⁵ Pt- ³¹ P)=2919Hz)
4~	-22.9(lH,t,l4Hz,Pt-H)* 2.98(2H,d,7Hz,CH ₂) 4.95(lH,d,5Hz,=CH ₂) 5.00(lH,d,5Hz,=CH ₂) 6.68(lH,m,-CH ₂ CH=CH ₂)	* 43.82(-CH ₂ CH=CH 114.31(=CH ₂) 136.78(CH) 174.51(C=O)	¹ 2) 46.5 (J(¹⁹⁵ Pt- ³¹ P)=2916Hz)

a) Data for PCy_3 in ^{l}H - and $^{l3}C{^{l}H}$ -NMR are omitted. b) * With satellites $(J(^{195}Pt-^{31}P)=1144Hz)$. ** With satellites (J=1146Hz). In CD₂Cl₂ at room temperature.

Tables 1 and 2 summarize analytical and spectral data of complexes 1-4. All the data support the formulation of the complexes shown in Eq. 1 and Table 1. The appearance of M-H signals of 1, 3, and 4 as triplets in ¹H-NMR reveals that they have <u>trans</u>-configulations. As for 2, its configulation has not been determined due to a rapid exchange between the PCy₃ ligand in 2 and free PCy₃ partly liberated into the solution even at -80 °C. The signals of olefinic protons and carbons of unsaturated acids (methacrylic acid and 1-butenoic acid) are scarecely shifted in the ¹H- and ¹³C{¹H}-NMR spectra, respectively, by the oxidative addition to Pt, indicating that the C=C double bond in the OCOR ligand does not coordinate to Pt though the coordination is not sterically hindered. Appearance of v(C=O) bands of complexes 3 and 4 at higher frequencies than 1600 cm⁻¹ indicates that the OCOR ligand binds to Pt through one oxygen atom.

Elimination of HY from the Complexes.

When CO (1 atm) was introduced into a CH_2Cl_2 solution of 1 at room temperature, a smooth elimination of succinimide took place accompanied by formation of nickel carbonyl complexes (mainly Ni(CO)₂(PCy₃)₂),

 $1 + CO \xrightarrow{r.t., 4h}$ succinimide (91%) + Ni-CO complexes (3)

Addition of maleic anhydride also causes the elimination of succinimide (yield = 60%). The Pd and Pt hydride complexes also undergo similar elimination reactions on addition of CO to release succinimide and the corresponding unsaturated carboxylic acid, respectively. Similar inductive effects of π -acid on the elimination of R-R, RCOOR', and RCOOCOR' from dialkyl⁷,⁷) acyl(alkoxo)-,⁸) and acyl(carboxylato)nickel⁹) complexes, respectively, have been reported. Table 3 summarizes the results of the elimination reactions.

Table 3.	Elimination of H π -Acids. ^{a)}	Y from MH	(Y)L Ind n	uced by
Complex	π-Acid		$\frac{\texttt{Time}}{\texttt{h}}$	Yield of HY
1~	CO		4	91
1 2	maleic anh	ydride	24	60
2	CO		24	85
3	СО		24	29
a) At roo	om temperature.	Excess amo	ounts of	π -acids per

complexes were added. The Ni complex, 1, reacts with CO more smoothly than the Pd and Pt complexes, 2 and 3, in accord with a usually observed trend in reactions of Ni, Pd, and Pt complexes

reactions.

Complex 1 has catalytic activities to initiate polymerization of vinyl monomers such as acrylnitrile, methyl methacrylate, and styrene.

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